Supporting Information for:

# Proton-Hydride Tautomerism in Hydrogen Evolution Catalysis

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**Figure S1.** $^{1}$H NMR spectrum of **3** with excess $[Et_3NH]^{+}Br^{-}$.

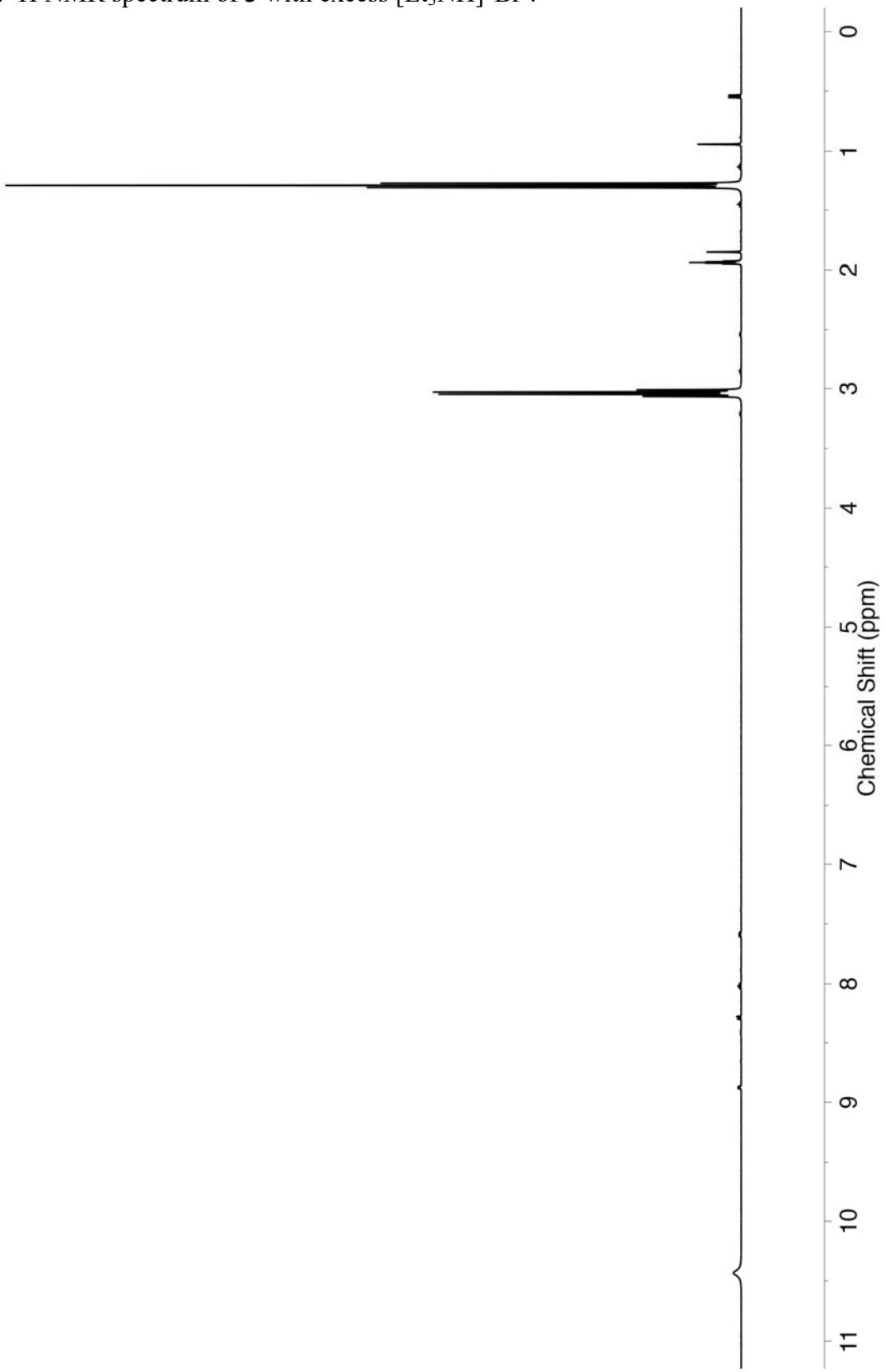


**Figure S2.** $^{1}$H NMR spectrum of **3** with excess $[Et_3NH]^{+}Br^{-}$. * indicates a small impurity of free 2,2′-bipyridyl. # is adventitious hexane from glovebox atmosphere.

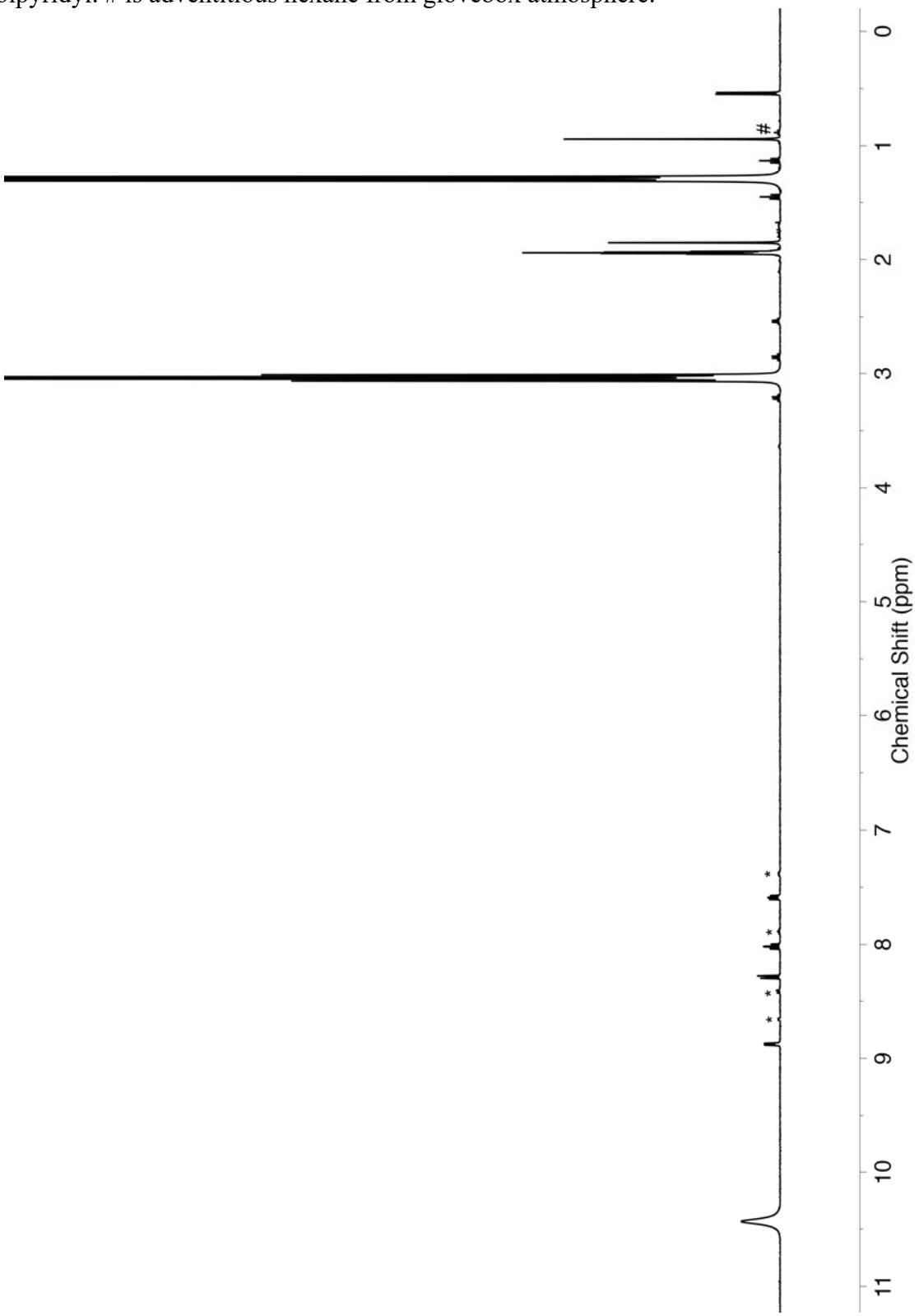


**Figure S3.** Alkyl region of the $^{1}$H NMR spectrum of **3** with excess $[Et_3NH]^{+}Br^{-}$. This region highlights the peaks corresponding to Rh-bound Cp*H.

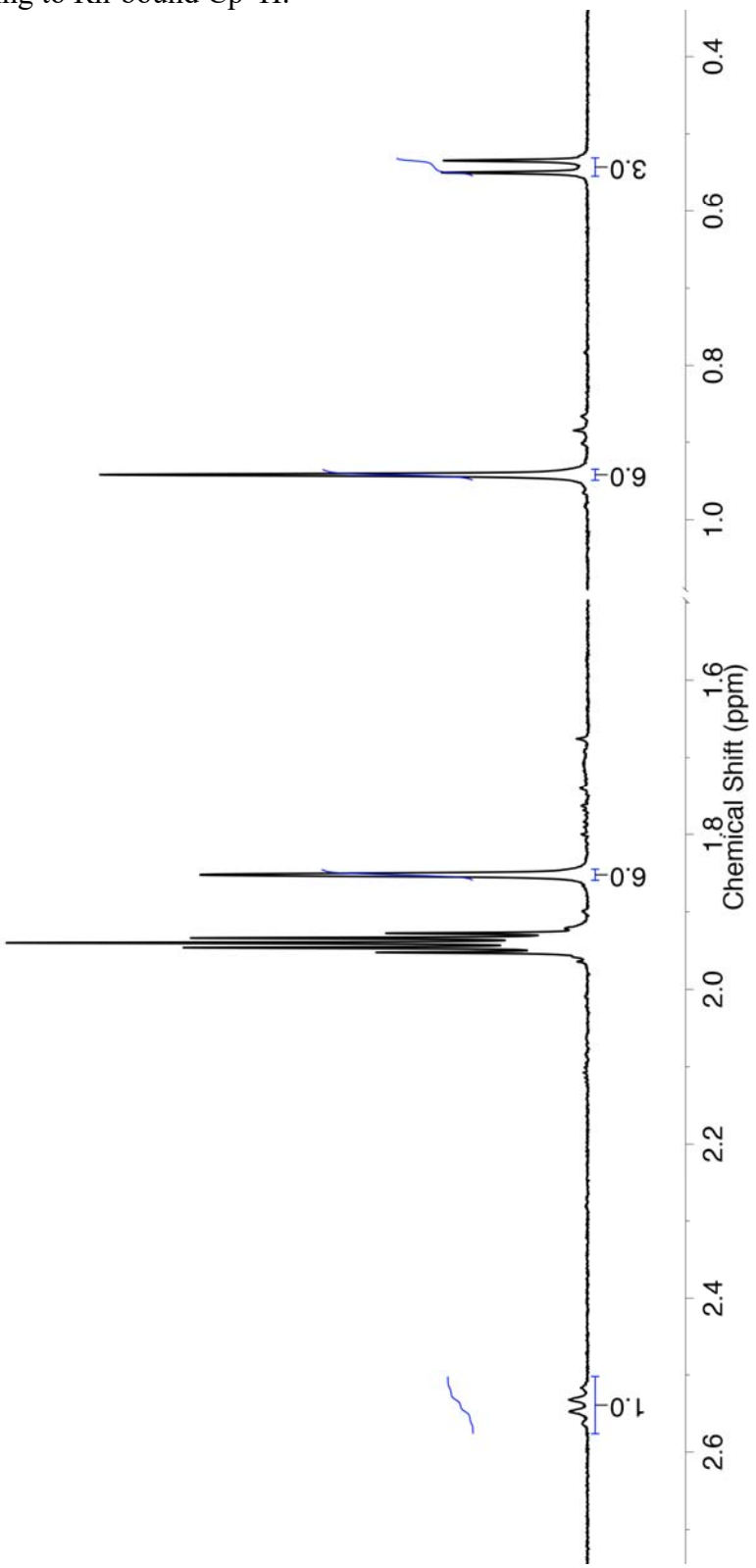


**Figure S4.** $^{13}C$ NMR spectrum of **3** with excess $[Et_3NH]^+Br^-$. * is MeCN solvent residual. # is $[Et_3NH]^+$.

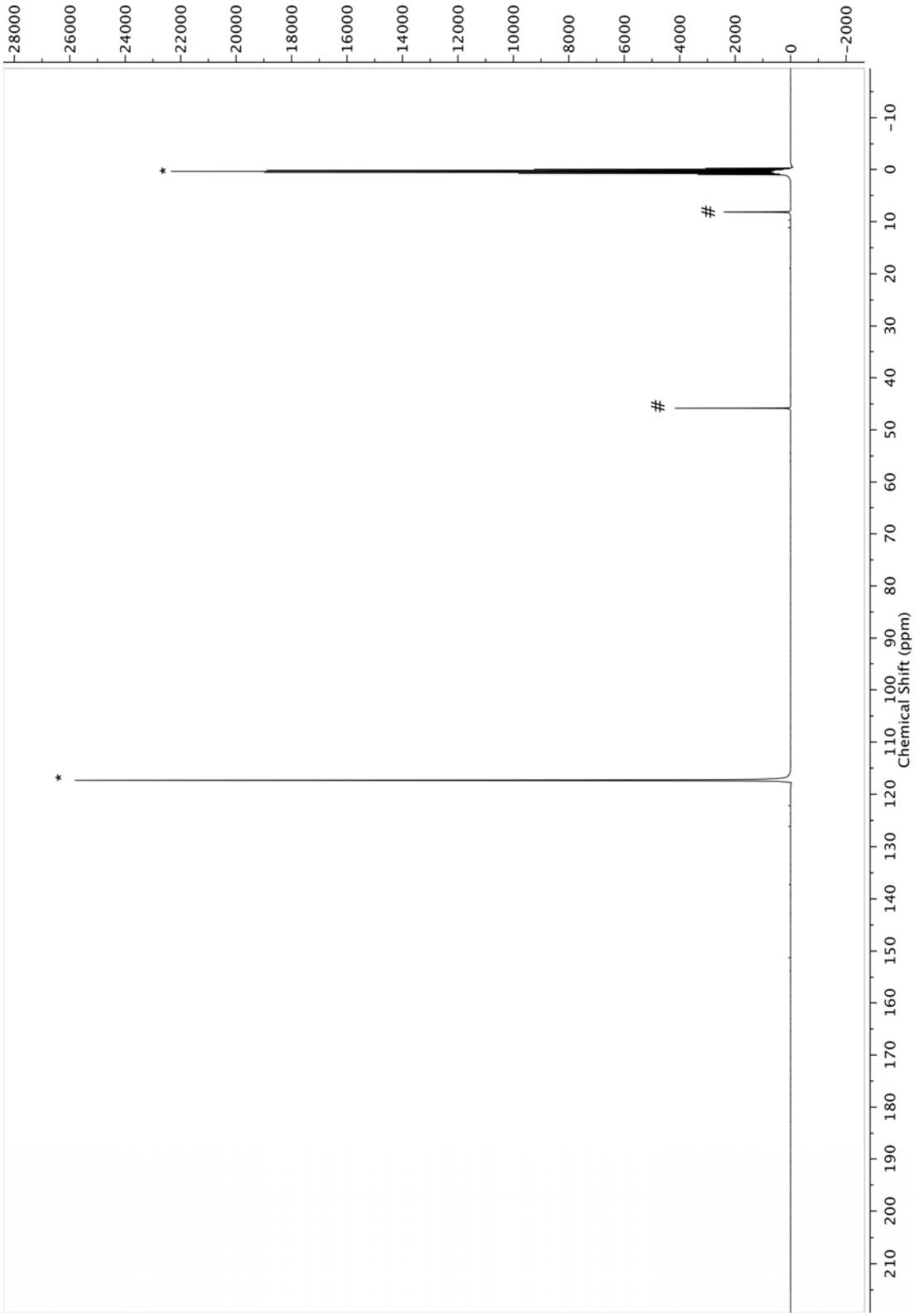


**Figure S5.** $^{13}C$ NMR spectrum of **3** with excess $[Et_3NH]^+Br^-$.

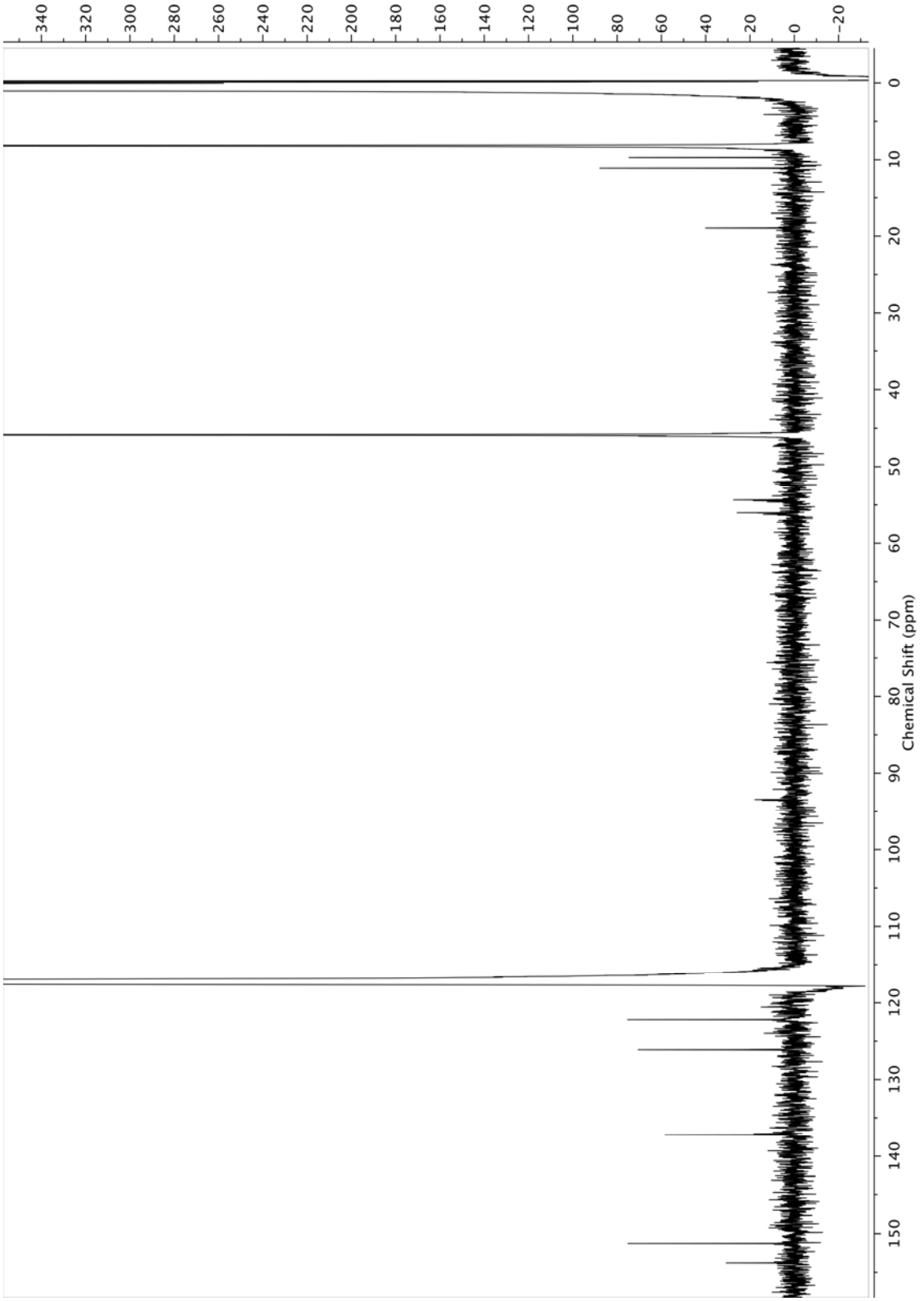


**Figure S6.** Comparison of $^{1}$H NMR spectra of **4** before and after addition of ~2 eq. of $[DMF{\cdot}H]^{+}OTf^{-}$. $ is *1,3,5*-$(OMe)_3C_6H_3$ internal standard. # is $[Et_3NH]^{+}/Et_3N$. *D* is dimethyformamide. * is **4**. * is dihydrogen. * is $[Cp^{*}Rh^{III}]$.

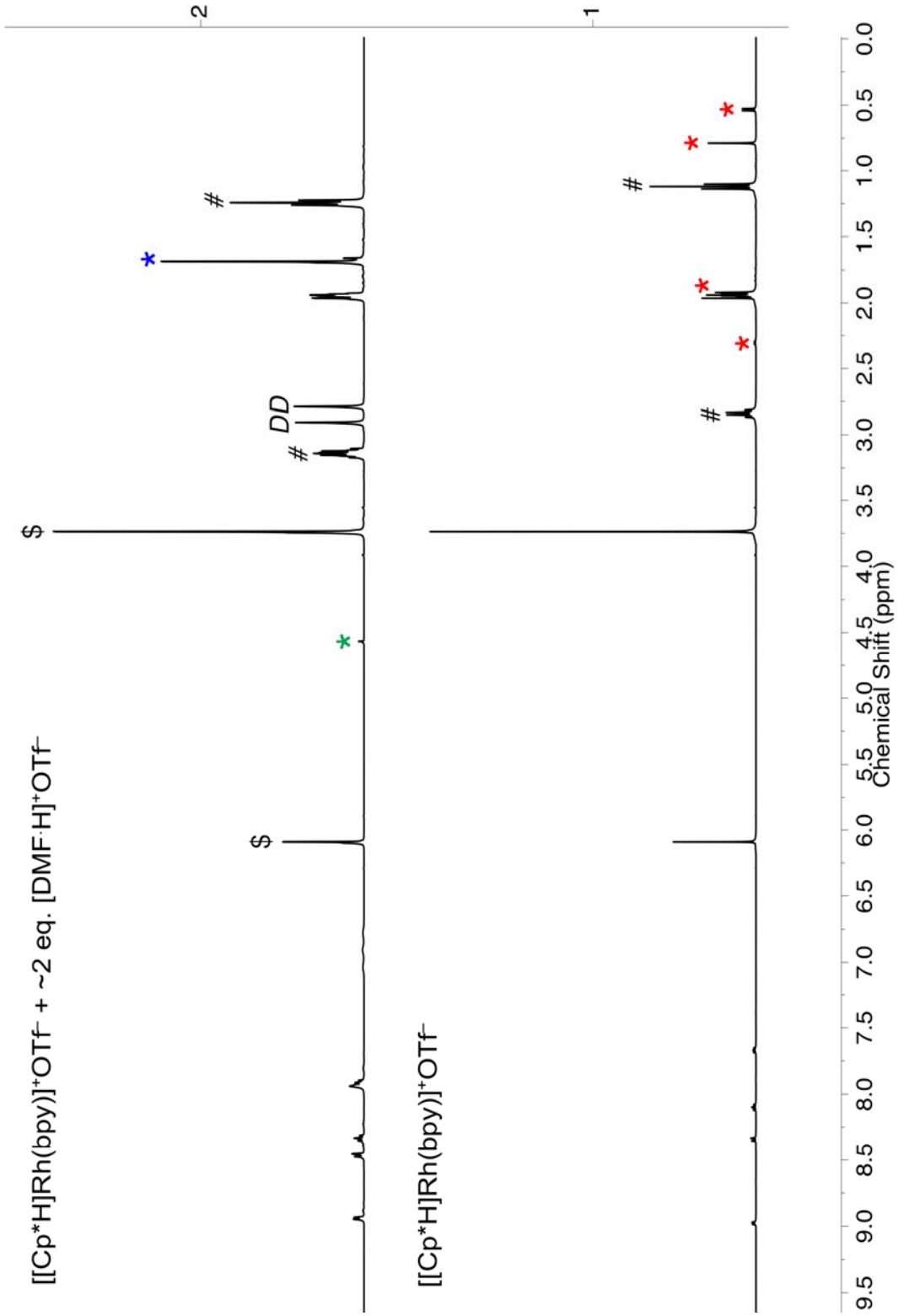


**Figure S7.** Comparison of $^{1}$H NMR spectra in the alkyl region of **4** before and after addition of ~2 eq. of $[DMF{\cdot}H]^{+}OTf^{-}$. # is $[Et_3NH]^{+}/Et_3N$. *D* is dimethyformamide.
* is **4**. * is dihydrogen. * is $[Cp^{*}Rh^{III}]$.

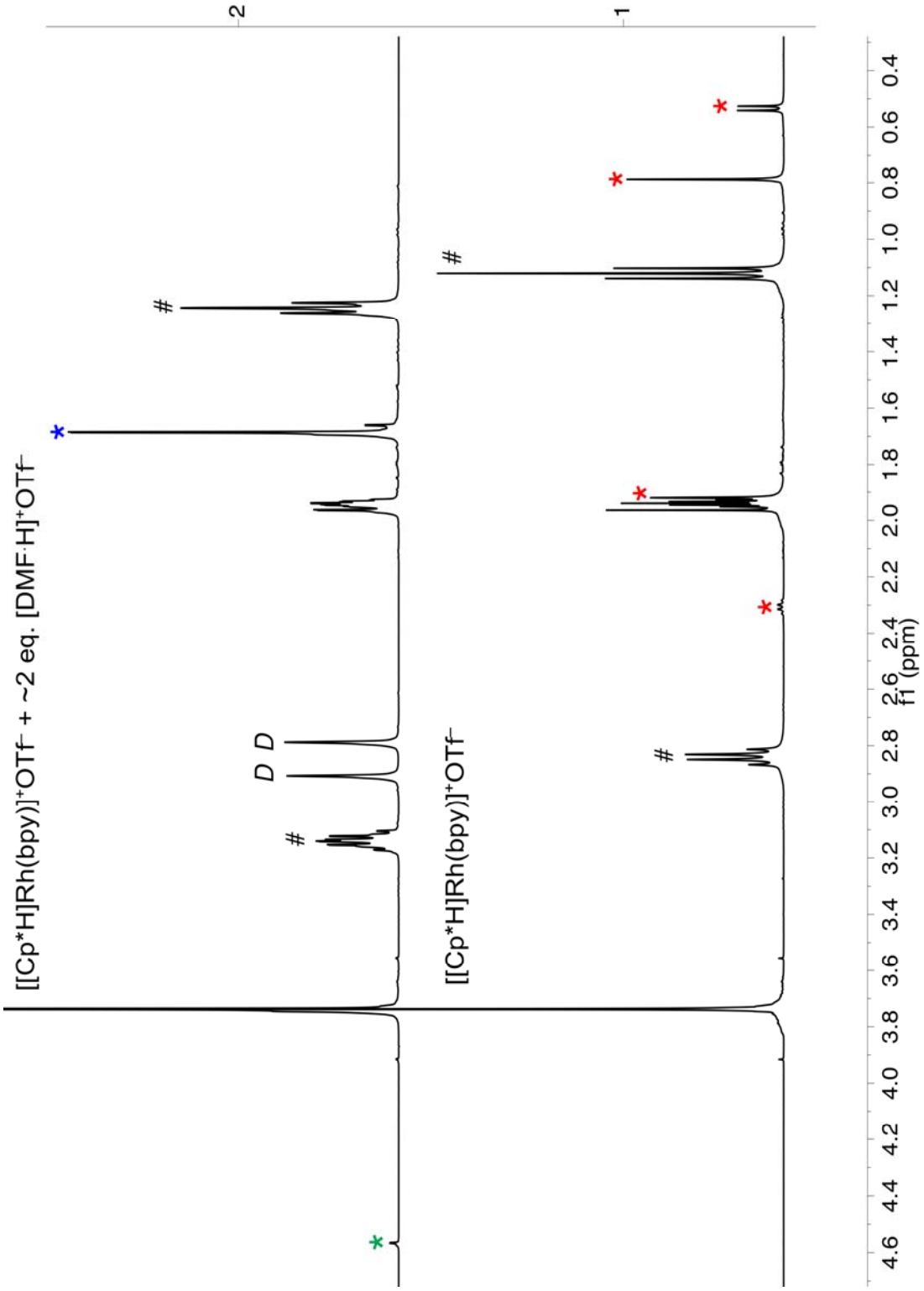


**Figure S8**. Gas chromatography data for determination of evolved $H_2$ evolution upon progressive additions of 1 eq. of $[Et_3NH]^+$ $OTf^-$, 1 eq. of $[DMF{\cdot}H]^+OTf^-$, and a further 1 eq. of $[DMF{\cdot}H]^+OTf^-$ to **1**.

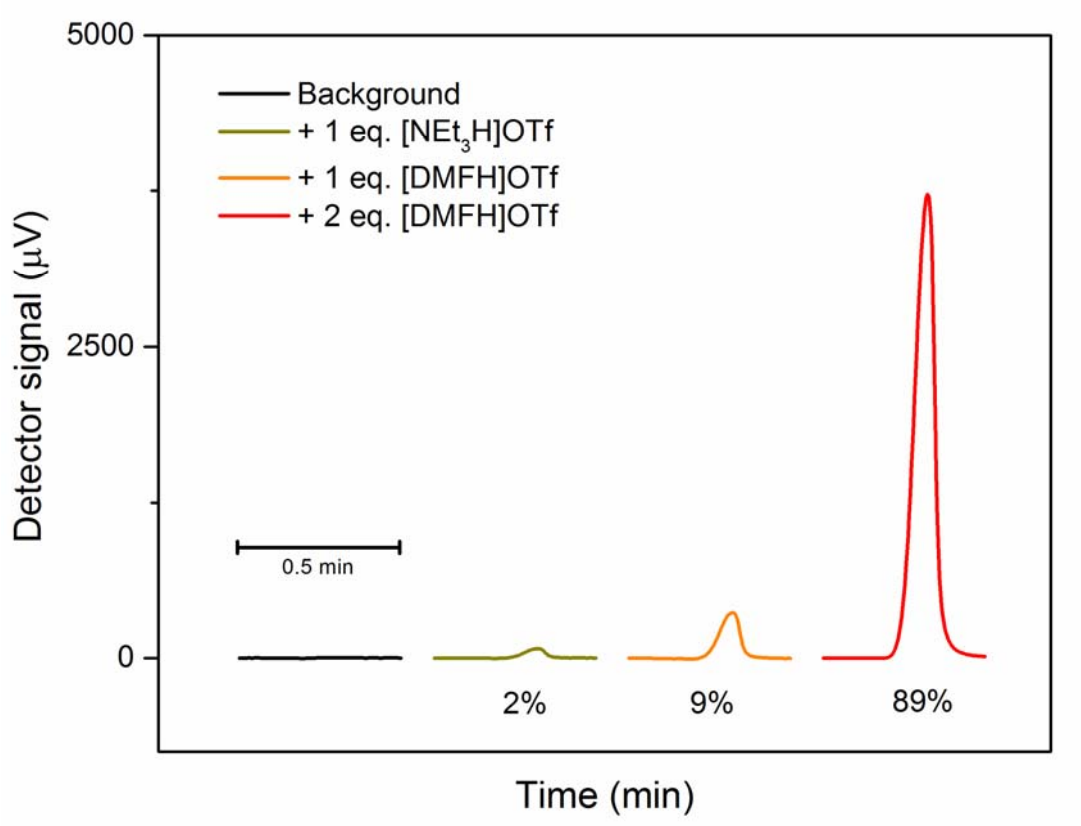


**Figure S9.** Gas chromatography data for determination of evolved $H_2$ evolution upon progressive additions of 1 eq. of $[Et_3NH]^+$ $OTf^-$, 1 eq. of $[DMF{\cdot}H]^+OTf^-$, and a further 1 eq. of $[DMF{\cdot}H]^+OTf^-$ to **2**.

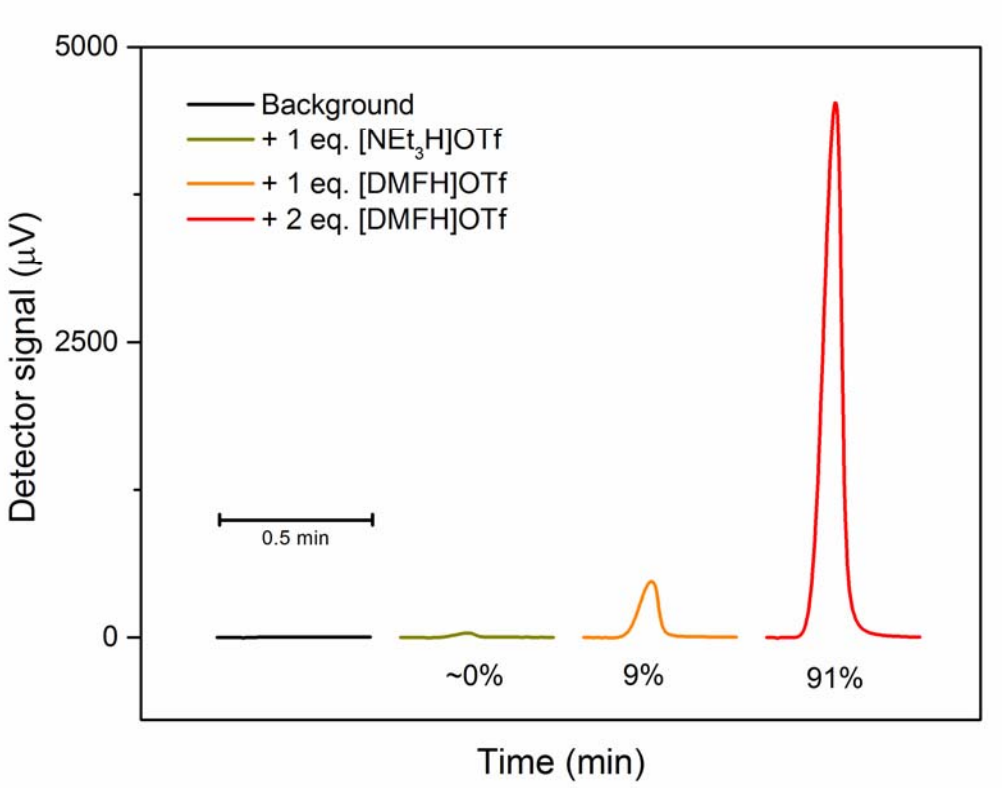


**Figure S10.** Absorption spectra of **1** and **3** in MeCN.

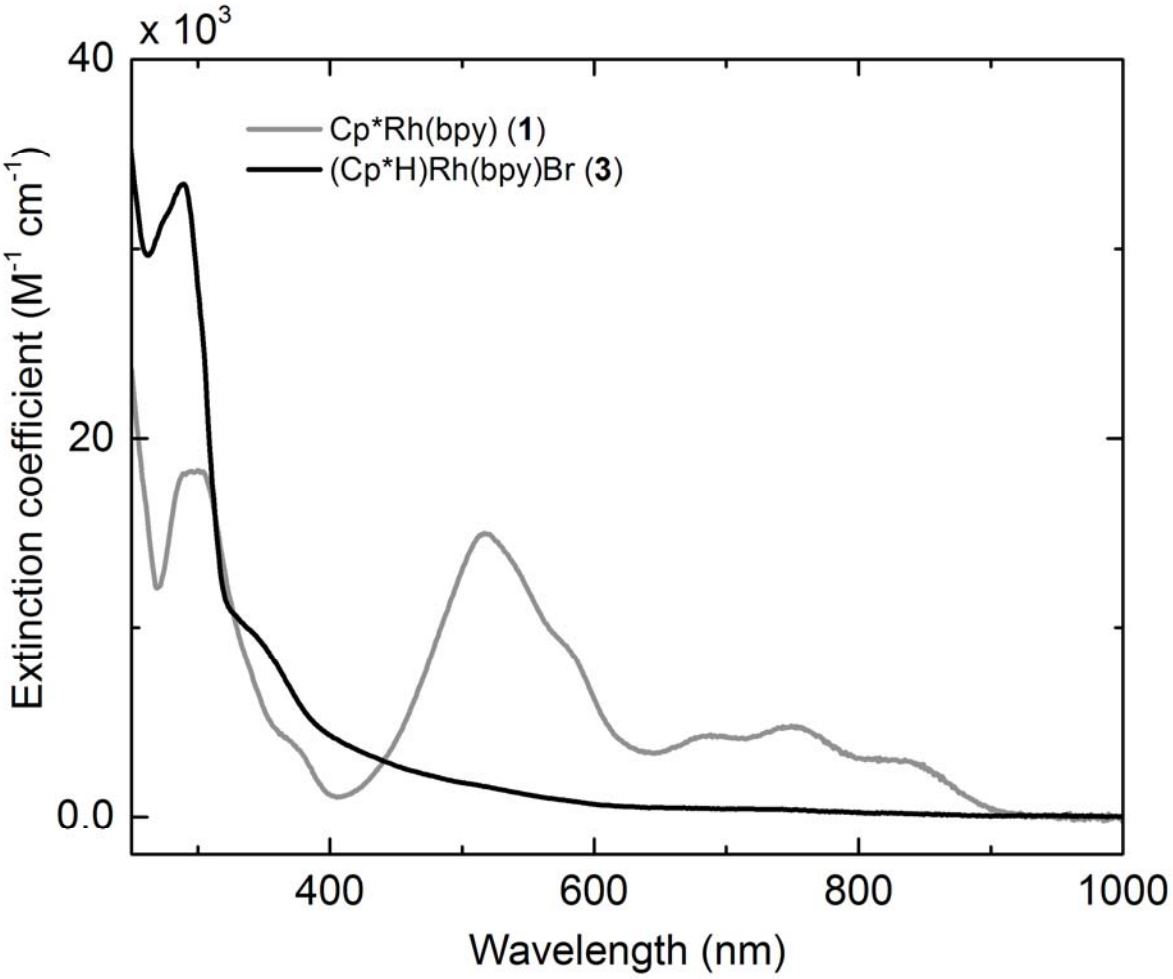


**Figure S11.** Absorption spectra of **2**, (Cp*H)Rh(phen)Br, and $[Cp^*Rh(phen)]^+$. $[Cp^*Rh(phen)]^+$ was generated by treatment of (Cp*H)Rh(phen)Br with $[DMF \cdot H]^+OTf^-$.

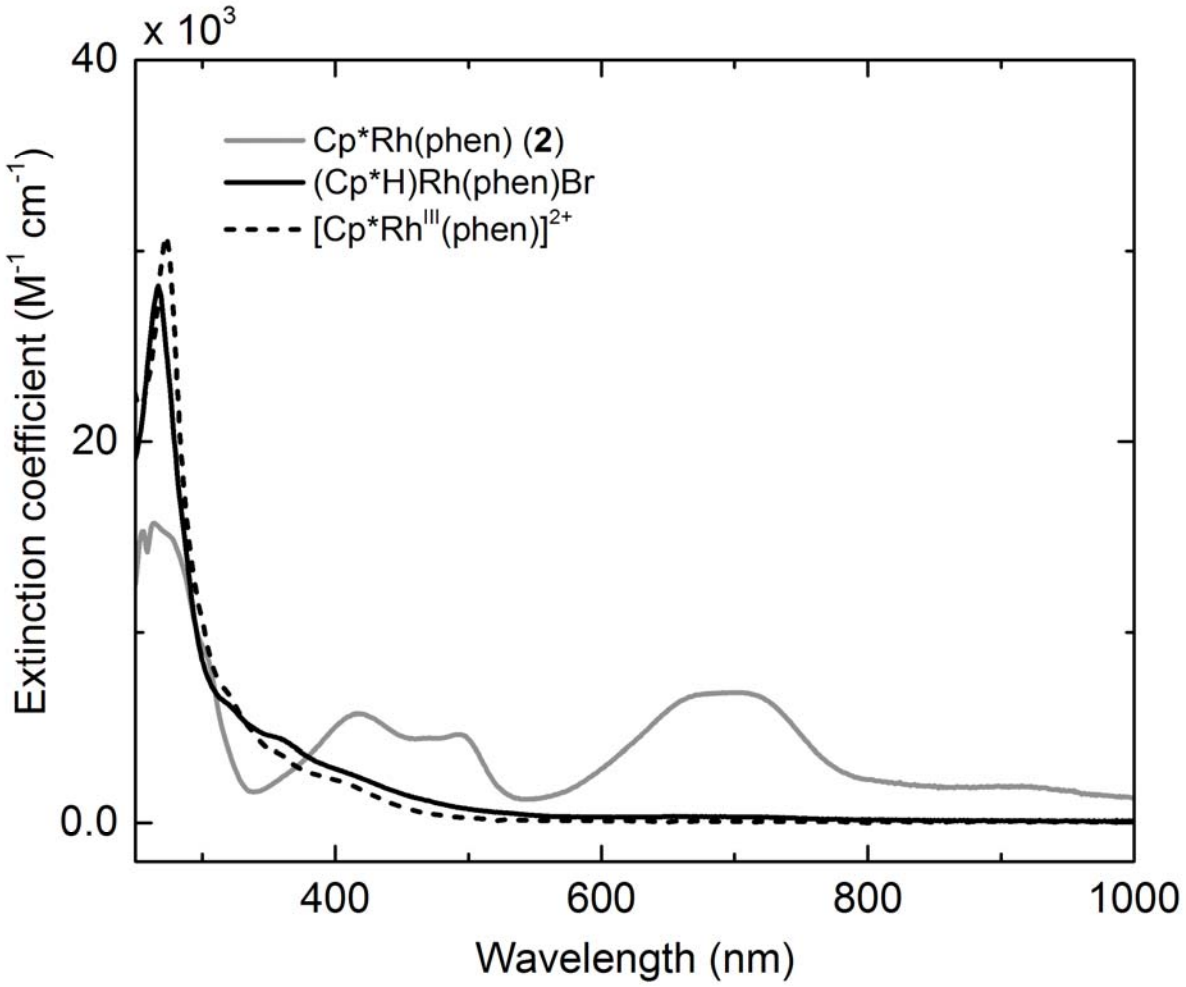
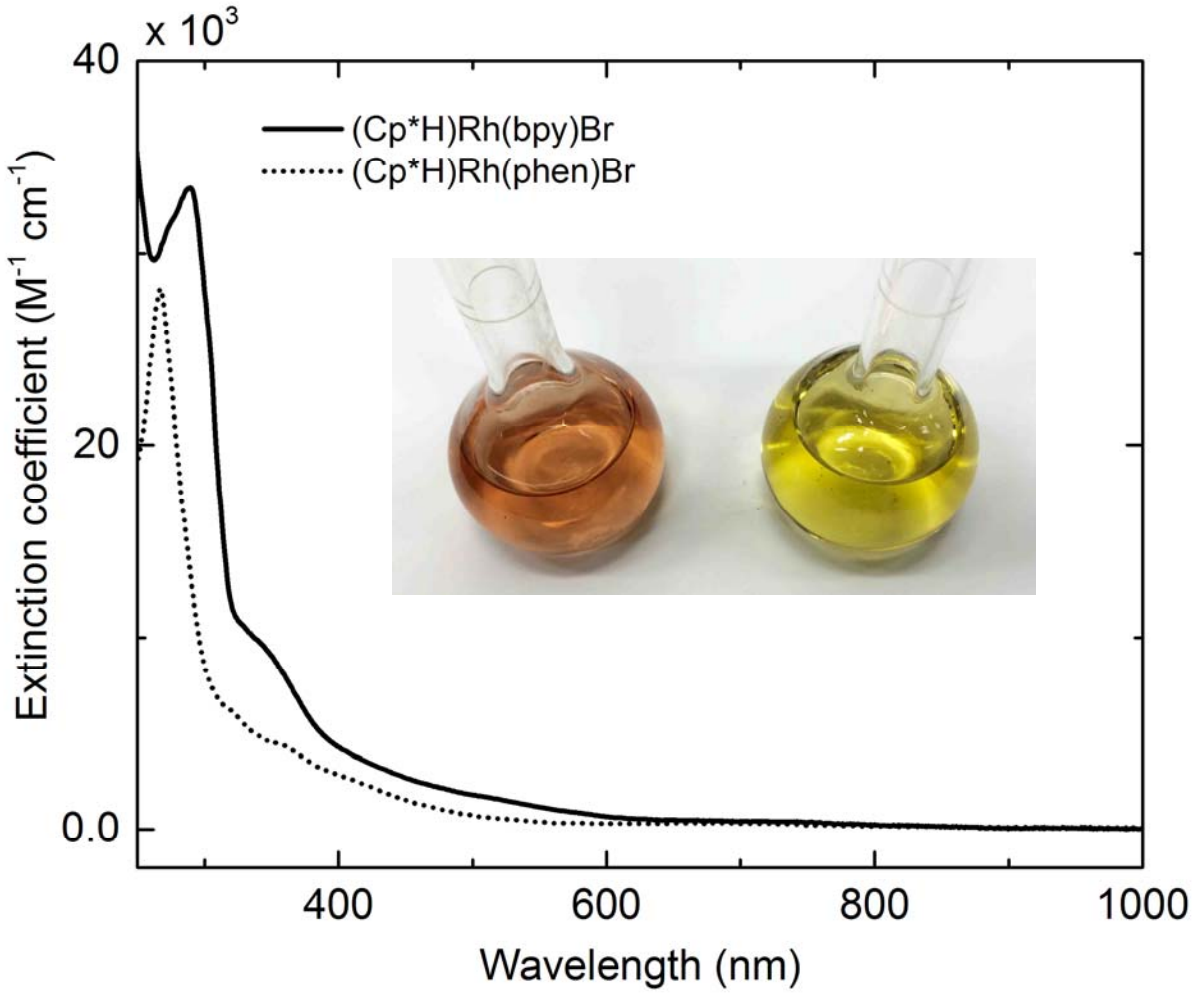


**Figure S12.** Absorption spectra of (Cp*H)Rh(bpy)Br and (Cp*H)Rh(phen)Br.



## X-ray Crystal Structure Data

**Table S1.** Crystal data and structure refinement for **3**.

| | |
|---|---|
| **Chemical Data** | |
| Chemical formula | $C_{20}\ H_{24}\ Br\ N_2\ Rh\ C_2\ H_3\ N$ |
| Formula weight | 516.28 |
| Crystallization solvent | Acetonitrile |
| Crystal habit | Block |
| Crystal size | 0.35 x 0.15 x 0.15 $mm^3$ |
| Crystal color | Orange |
| **Data Collection** | |
| Type of diffractometer | Bruker D8 VENTURE Kappa Duo PHOTON 100 |
| Wavelength | 0.71073 |
| Data collection temperature | 100(2) K |
| Crystal system | Orthorhombic |
| Space group | Pnma |
| Cell dimensions | a = 22.003(2) Å α = 90° |
| | b = 12.3185(10) Å β = 90° |
| | c = 7.8446(7) Å γ = 90° |
| Cell volume | 2126.3(3) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.613 $mg/cm^3$ |
| F(000) | 1040 |
| q range for data collection | 2.757 to 36.302° |
| Index ranges | $-36 \le h \le 36$ ; $-20 \le k \le 20$ ; $-13 \le l \le 12$ |
| Data collection scan type | φ and ω scans |
| Reflections collected | 28033 |
| Absorption coefficient | 2.694 |
| Min. and max. transmission | 0.6266 and 0.7471 |
| **Refinement** | |
| Structure solution program | SHELXS-2013/1 (Sheldrick, 2012) |
| Structure refinement program | SHELXL-2014/7 (Sheldrick, 2014) |
| Refinement method | Full matrix least-squares on $F^2$ |
| Data/restraints/parameters | 5308 / 1 / 139 |
| Goodness of fit | 1.009 |
| Final R indices | R1 = 0.0316, wR2 = 0.0545 |
| [I > 2σ (I), 3970] | |
| R indices (all data) | R1 = 0.0559, wR2 = 0.0603 |
| Weighting scheme | Calculated |
| | $w = 1 / [\sigma^2 F_o^2 + (0.0222P)^2 + 1.0579P]$ |
| | $P = (F_o^2 + 2F_c^2) / 3$ |
| Max shift/error | 0.002 |
| Average shift/error | 0.000 |
| Largest diff. peak and hole | 0.660 and –0.754 $e^-/Å^3$ |

**Table S2.** Selected bond lengths (Å) for **3**.

| | |
|---|---|
| Rh(1)-C(3)#1 | 2.1122(15) |
| Rh(1)-C(3) | 2.1122(15) |
| Rh(1)-N(1)#1 | 2.1165(12) |
| Rh(1)-N(1) | 2.1165(12) |
| Rh(1)-C(2)#1 | 2.1328(14) |
| Rh(1)-C(2) | 2.1328(14) |
| Rh(1)-Br(1) | 2.6512(3) |
| N(1)-C(11) | 1.3415(19) |
| N(1)-C(15) | 1.3574(18) |
| C(1)-C(2) | 1.523(2) |
| C(1)-C(2)#1 | 1.523(2) |
| C(1)-C(6) | 1.537(3) |
| C(1)-H(1) | 0.982(16) |
| C(2)-C(3) | 1.442(2) |
| C(2)-C(7) | 1.501(2) |
| C(3)-C(3)#1 | 1.442(3) |
| C(3)-C(8) | 1.497(2) |
| C(6)-H(6A) | 0.98 |
| C(6)-H(6B) | 0.98 |
| C(6)-H(6C) | 0.98 |
| C(7)-H(7A) | 0.98 |
| C(7)-H(7B) | 0.98 |
| C(7)-H(7C) | 0.98 |
| C(8)-H(8A) | 0.98 |
| C(8)-H(8B) | 0.98 |
| C(8)-H(8C) | 0.98 |
| C(11)-C(12) | 1.386(2) |
| C(11)-H(11) | 0.95 |
| C(12)-C(13) | 1.392(2) |
| C(12)-H(12) | 0.95 |
| C(13)-C(14) | 1.383(2) |
| C(13)-H(13) | 0.95 |
| C(14)-C(15) | 1.395(2) |
| C(14)-H(14) | 0.95 |
| C(15)-C(15)#1 | 1.475(3) |
| N(1S)-C(1S) | 1.136(3) |
| C(1S)-C(2S) | 1.464(4) |
| C(2S)-H(2S1) | 0.98 |
| C(2S)-H(2S2) | 0.98 |
| C(2S)-H(2S3) | 0.98 |

**Table S3.** Selected bond angles (°) for **3**.

| | | | |
|---|---|---|---|
| C(3)#1-Rh(1)-C(3) | 39.91(8) | H(7A)-C(7)-H(7C) | 109.5 |
| C(3)#1-Rh(1)-N(1)#1 | 107.27(5) | H(7B)-C(7)-H(7C) | 109.5 |
| C(3)-Rh(1)-N(1)#1 | 136.23(5) | C(3)-C(8)-H(8A) | 109.5 |
| C(3)#1-Rh(1)-N(1) | 136.23(5) | C(3)-C(8)-H(8B) | 109.5 |
| C(3)-Rh(1)-N(1) | 107.27(5) | H(8A)-C(8)-H(8B) | 109.5 |
| N(1)#1-Rh(1)-N(1) | 77.09(6) | C(3)-C(8)-H(8C) | 109.5 |
| C(3)#1-Rh(1)-C(2)#1 | 39.72(6) | H(8A)-C(8)-H(8C) | 109.5 |
| C(3)-Rh(1)-C(2)#1 | 66.03(6) | H(8B)-C(8)-H(8C) | 109.5 |
| N(1)#1-Rh(1)-C(2)#1 | 109.25(5) | N(1)-C(11)-C(12) | 123.02(14) |
| N(1)-Rh(1)-C(2)#1 | 172.90(5) | N(1)-C(11)-H(11) | 118.5 |
| C(3)#1-Rh(1)-C(2) | 66.03(6) | C(12)-C(11)-H(11) | 118.5 |
| C(3)-Rh(1)-C(2) | 39.72(6) | C(11)-C(12)-C(13) | 118.69(14) |
| N(1)#1-Rh(1)-C(2) | 172.90(5) | C(11)-C(12)-H(12) | 120.7 |
| N(1)-Rh(1)-C(2) | 109.25(5) | C(13)-C(12)-H(12) | 120.7 |
| C(2)#1-Rh(1)-C(2) | 64.24(8) | C(14)-C(13)-C(12) | 118.84(14) |
| C(3)#1-Rh(1)-Br(1) | 138.05(4) | C(14)-C(13)-H(13) | 120.6 |
| C(3)-Rh(1)-Br(1) | 138.05(4) | C(12)-C(13)-H(13) | 120.6 |
| N(1)#1-Rh(1)-Br(1) | 85.18(3) | C(13)-C(14)-C(15) | 119.50(14) |
| N(1)-Rh(1)-Br(1) | 85.18(3) | C(13)-C(14)-H(14) | 120.3 |
| C(2)#1-Rh(1)-Br(1) | 98.36(4) | C(15)-C(14)-H(14) | 120.3 |
| C(2)-Rh(1)-Br(1) | 98.36(4) | N(1)-C(15)-C(14) | 121.57(13) |
| C(11)-N(1)-C(15) | 118.37(12) | N(1)-C(15)-C(15)#1 | 115.36(8) |
| C(11)-N(1)-Rh(1) | 125.36(10) | C(14)-C(15)-C(15)#1 | 123.05(9) |
| C(15)-N(1)-Rh(1) | 115.59(9) | N(1S)-C(1S)-C(2S) | 179.3(3) |
| C(2)-C(1)-C(2)#1 | 96.24(16) | C(1S)-C(2S)-H(2S1) | 109.5 |
| C(2)-C(1)-C(6) | 115.50(12) | C(1S)-C(2S)-H(2S2) | 109.5 |
| C(2)#1-C(1)-C(6) | 115.50(12) | H(2S1)-C(2S)-H(2S2) | 109.5 |
| C(2)-C(1)-H(1) | 108.4(10) | C(1S)-C(2S)-H(2S3) | 109.5 |
| C(2)#1-C(1)-H(1) | 108.4(10) | H(2S1)-C(2S)-H(2S3) | 109.5 |
| C(6)-C(1)-H(1) | 111.6(16) | H(2S2)-C(2S)-H(2S3) | 109.5 |
| C(3)-C(2)-C(7) | 125.65(14) | | |
| C(3)-C(2)-C(1) | 108.78(13) | | |
| C(7)-C(2)-C(1) | 120.67(13) | | |
| C(3)-C(2)-Rh(1) | 69.37(8) | | |
| C(7)-C(2)-Rh(1) | 126.60(11) | | |
| C(1)-C(2)-Rh(1) | 91.19(10) | | |
| C(3)#1-C(3)-C(2) | 106.65(9) | | |
| C(3)#1-C(3)-C(8) | 125.66(9) | | |
| C(2)-C(3)-C(8) | 127.68(14) | | |
| C(3)#1-C(3)-Rh(1) | 70.04(4) | | |
| C(2)-C(3)-Rh(1) | 70.91(8) | | |
| C(8)-C(3)-Rh(1) | 124.98(10) | | |
| C(1)-C(6)-H(6A) | 109.5 | | |
| C(1)-C(6)-H(6B) | 109.5 | | |

| | |
|---|---|
| H(6A)-C(6)-H(6B) | 109.5 |
| C(1)-C(6)-H(6C) | 109.5 |
| H(6A)-C(6)-H(6C) | 109.5 |
| H(6B)-C(6)-H(6C) | 109.5 |
| C(2)-C(7)-H(7A) | 109.5 |
| C(2)-C(7)-H(7B) | 109.5 |
| H(7A)-C(7)-H(7B) | 109.5 |
| C(2)-C(7)-H(7C) | 109.5 |

**Calculated Geometries**

**1**

| | | | |
|---|---|---|---|
| C1 | -1.5276452401 | 3.2504532630 | -0.9672614965 |
| N2 | -0.3545756073 | 3.9643919482 | -1.1118599572 |
| C3 | -0.1517586588 | 4.6164717293 | -2.2899106083 |
| C4 | -1.0504047947 | 4.5959085194 | -3.3335422658 |
| C5 | -2.2495726333 | 3.8681920231 | -3.1935991315 |
| C6 | -2.4753119239 | 3.2005214630 | -2.0064562358 |
| H8 | 0.7814112203 | 5.1610051368 | -2.3634527319 |
| H9 | -0.8240096777 | 5.1393076095 | -4.2452231667 |
| H10 | -2.9783274048 | 3.8313607889 | -3.9969272089 |
| H11 | -3.3885765928 | 2.6320961091 | -1.8669532653 |
| C12 | -1.7096138099 | 1.4475675615 | 2.8191679405 |
| C13 | -2.8016938316 | 1.2351379989 | 1.9531354815 |
| C14 | -2.7654356666 | 1.8153328176 | 0.7012699869 |
| C15 | -1.6633484711 | 2.5975751426 | 0.3082215200 |
| N16 | -0.5961055370 | 2.8013909132 | 1.1615804168 |
| C17 | -0.6519797012 | 2.2195180948 | 2.3920165676 |
| H18 | -1.6875039078 | 1.0144785948 | 3.8140085692 |
| H19 | -3.6497542068 | 0.6320960030 | 2.2612805428 |
| H20 | -3.5898080328 | 1.6726316541 | 0.0107700244 |
| H22 | 0.2028395293 | 2.4014525555 | 3.0304388701 |
| Rh21 | 0.9196304928 | 3.9697047762 | 0.4707677239 |
| C22 | 2.5730087370 | 4.0764234721 | 2.0241121382 |
| C23 | 2.0726088230 | 5.4230460483 | 1.8654263536 |
| C24 | 2.2967822608 | 5.8009820705 | 0.5091068100 |
| C25 | 2.9835518668 | 4.7080077334 | -0.1544158866 |
| C26 | 3.2088789354 | 3.6692747555 | 0.7996084215 |
| C34 | 2.6504321159 | 3.3290967760 | 3.3261278999 |
| H35 | 2.5939229796 | 2.2459411862 | 3.1783082024 |
| H36 | 3.5973086721 | 3.5353325749 | 3.8434076606 |
| H37 | 1.8462049694 | 3.6189024704 | 4.0095092301 |
| C38 | 1.4650618203 | 6.2706289958 | 2.9451211616 |
| H39 | 0.7861663670 | 7.0214913065 | 2.5313415104 |
| H40 | 0.8894507266 | 5.6695806339 | 3.6556354264 |
| H41 | 2.2341736699 | 6.8051677358 | 3.5212801022 |

| | | | |
|---|---|---|---|
| C42 | 1.9820754997 | 7.1355507776 | -0.1041686855 |
| H43 | 1.6799520440 | 7.0432092931 | -1.1524686735 |
| H44 | 1.1665306023 | 7.6363075594 | 0.4249559077 |
| H45 | 2.8530073894 | 7.8052254750 | -0.0792837621 |
| C46 | 3.5310091705 | 4.7386440567 | -1.5532077995 |
| H47 | 3.5156332176 | 3.7468929404 | -2.0149722241 |
| H48 | 2.9630655226 | 5.4135515743 | -2.2003716278 |
| H49 | 4.5711392829 | 5.0920720154 | -1.5644623866 |
| C50 | 3.9918303280 | 2.4073159182 | 0.5826268909 |
| H51 | 3.9544132433 | 2.0843698011 | -0.4619240787 |
| H52 | 5.0519950447 | 2.5392182084 | 0.8459498154 |
| H53 | 3.6079191359 | 1.5841646333 | 1.1927467765 |

**4**

| | | | |
|---|---|---|---|
| C1 | 0.1692043636 | 1.3213366236 | 0.7155259131 |
| N2 | -0.6066722083 | 2.4195725431 | 0.9118302459 |
| C3 | -1.3709526050 | 2.4902210235 | 2.0146150722 |
| C4 | -1.4039222404 | 1.4850324815 | 2.9753977370 |
| C5 | -0.6116694469 | 0.3558332419 | 2.7832208491 |
| C6 | 0.1811797393 | 0.2750771760 | 1.6418433207 |
| H8 | -1.9705878799 | 3.3851667560 | 2.1185298479 |
| H9 | -2.0378890786 | 1.5920135066 | 3.8485955458 |
| H10 | -0.6089958713 | -0.4517995168 | 3.5082233618 |
| H11 | 0.8015723416 | -0.5975815806 | 1.4789561340 |
| C12 | 2.4232555605 | 1.4894859232 | -2.8676442798 |
| C13 | 2.5677213995 | 0.3614217116 | -2.0636378369 |
| C14 | 1.8384938893 | 0.2789612538 | -0.8808067381 |
| C15 | 0.9805264074 | 1.3223133179 | -0.5226289083 |
| N16 | 0.8471337397 | 2.4197684369 | -1.3128239644 |
| C17 | 1.5524482959 | 2.4920165428 | -2.4541041485 |
| H18 | 2.9699079451 | 1.5975474108 | -3.7978745000 |
| H19 | 3.2364816109 | -0.4438963707 | -2.3501495262 |
| H20 | 1.9407568594 | -0.5924300566 | -0.2458749413 |
| H22 | 1.4052887941 | 3.3861372100 | -3.0458213822 |
| Rh21 | -0.5006152580 | 3.9056081038 | -0.6064126797 |
| C22 | -0.1475302920 | 5.9524963964 | -1.2596522553 |
| C23 | -0.9465551777 | 5.9579399589 | -0.0288303704 |
| C24 | -2.1904540747 | 5.3504310863 | -0.3265706822 |
| C25 | -2.3910975247 | 5.3074047798 | -1.8382010555 |
| C26 | -0.9289504453 | 5.3420643235 | -2.2705093753 |
| C34 | 1.2167169751 | 6.5602862784 | -1.4006448519 |
| H35 | 1.7676679499 | 6.1300210612 | -2.2403537675 |
| H36 | 1.1307421945 | 7.6386318578 | -1.5858820986 |
| H37 | 1.8175251974 | 6.4259314190 | -0.4979904778 |
| C38 | -0.5172093866 | 6.5726594213 | 1.2705024674 |
| H39 | -1.0598095154 | 6.1487492646 | 2.1188333229 |

| | | | |
|---|---|---|---|
| H40 | 0.5518743180 | 6.4376765290 | 1.4511315379 |
| H41 | -0.7193985681 | 7.6514665800 | 1.2605753475 |
| C42 | -3.3477400067 | 5.1860876637 | 0.6140095263 |
| H43 | -3.8670318537 | 4.2368135889 | 0.4443548128 |
| H44 | -3.0516815227 | 5.2406994866 | 1.6648423463 |
| H45 | -4.0832956314 | 5.9847686851 | 0.4513888096 |
| C46 | -3.2403196212 | 6.4741196505 | -2.3956305929 |
| H47 | -3.2966612511 | 6.4249884223 | -3.4871075911 |
| H48 | -4.2633695212 | 6.4239576307 | -2.0121311387 |
| H49 | -2.8098916199 | 7.4401771444 | -2.1133447227 |
| C50 | -0.5437708222 | 5.1675148227 | -3.7098726851 |
| H51 | -0.9146009948 | 4.2173036873 | -4.1087133771 |
| H52 | -0.9893340438 | 5.9646471126 | -4.3193670140 |
| H53 | 0.5365077024 | 5.2169031354 | -3.8693157255 |
| H54 | -2.8674262975 | 4.3652381487 | -2.1435211128 |

**4H**

| | | | |
|---|---|---|---|
| C1 | -0.4752082896 | 1.1266614475 | 1.1307042442 |
| N2 | -1.1230698745 | 2.3078138503 | 0.9627991884 |
| C3 | -2.4331134849 | 2.3877825582 | 1.2522707101 |
| C4 | -3.1684362440 | 1.2949848994 | 1.6967844282 |
| C5 | -2.5182524753 | 0.0728198279 | 1.8589693257 |
| C6 | -1.1588539803 | -0.0081888318 | 1.5783668082 |
| H8 | -2.8894729665 | 3.3616359802 | 1.1277389197 |
| H9 | -4.2247778067 | 1.4083229750 | 1.9135435729 |
| H10 | -3.0580422397 | -0.8028378090 | 2.2044528359 |
| H11 | -0.6360610392 | -0.9475140277 | 1.7086641579 |
| C12 | 3.6580103544 | 1.3952718672 | 0.2706099412 |
| C13 | 3.1625948066 | 0.1561912226 | 0.6731164340 |
| C14 | 1.8071691994 | 0.0347535026 | 0.9595592731 |
| C15 | 0.9692622479 | 1.1472063798 | 0.8293029801 |
| N16 | 1.4618471717 | 2.3448930749 | 0.4231113172 |
| C17 | 2.7744890824 | 2.4630714919 | 0.1638988534 |
| H18 | 4.7089940506 | 1.5410364503 | 0.0466785403 |
| H19 | 3.8210043923 | -0.7010957613 | 0.7690014684 |
| H20 | 1.4072669265 | -0.9183955369 | 1.2831144022 |
| H22 | 3.1150043847 | 3.4486919948 | -0.1280161823 |
| Rh21 | 0.0549886205 | 3.9192248480 | 0.2517308349 |
| C22 | 0.9620623293 | 5.5733113533 | -0.9292893743 |
| C23 | -0.0541855686 | 6.1236544106 | -0.0779268117 |
| C24 | -1.3014050361 | 5.5284738806 | -0.4654305374 |
| C25 | -1.0719416055 | 4.7322048173 | -1.6765386448 |
| C26 | 0.3045436637 | 4.7592189666 | -1.9582653039 |
| C34 | 2.3992643815 | 6.0051893869 | -0.9640309747 |
| H35 | 3.0419717231 | 5.2545039639 | -1.4323022897 |
| H36 | 2.5057298917 | 6.9228501862 | -1.5565134508 |

| | | | |
|---|---|---|---|
| H37 | 2.7858933512 | 6.2145603092 | 0.0364479005 |
| C38 | 0.1379578208 | 7.1799972012 | 0.9712638246 |
| H39 | -0.5937036520 | 7.0896926290 | 1.7767366828 |
| H40 | 1.1341016109 | 7.1344015168 | 1.4159808377 |
| H41 | 0.0180955999 | 8.1738072877 | 0.5213672015 |
| C42 | -2.6514097486 | 5.9032102265 | 0.0728210864 |
| H43 | -3.3974464759 | 5.1267324773 | -0.1180397990 |
| H44 | -2.6221182983 | 6.0971484421 | 1.1480177086 |
| H45 | -3.0159095482 | 6.8155277714 | -0.4161942085 |
| C46 | -2.1514440242 | 4.0371635350 | -2.4510642663 |
| H47 | -1.7431869534 | 3.3074949327 | -3.1532717161 |
| H48 | -2.8495263168 | 3.5109703048 | -1.7921177407 |
| H49 | -2.7392621515 | 4.7614184180 | -3.0282690079 |
| C50 | 1.0171171462 | 4.1038119557 | -3.1032784854 |
| H51 | 0.4005571423 | 3.3423493572 | -3.5851423749 |
| H52 | 1.2844555734 | 4.8462834686 | -3.8652920815 |
| H53 | 1.9479427910 | 3.6254760253 | -2.7823565554 |
| H54 | 0.3641529419 | 4.1822293275 | 1.7575708548 |

**$[Et_3NH]^+$**

| | | | |
|---|---|---|---|
| N1 | -0.5831869008 | 0.1974570333 | 2.5785369573 |
| C2 | -0.6194123236 | -1.2481624957 | 2.8053133425 |
| C3 | 0.1582519783 | -2.0352139245 | 1.7489179443 |
| H4 | -1.6687444887 | -1.5625979345 | 2.7695587519 |
| H5 | -0.2472319078 | -1.5206786515 | 3.8138945569 |
| H6 | 0.0605696090 | -3.1114353758 | 1.9278624681 |
| H7 | -0.2246587180 | -1.8110604636 | 0.7486107939 |
| H8 | 1.2265498285 | -1.7964018587 | 1.7632595024 |
| C9 | 0.7535483325 | 0.7853637162 | 2.7820033122 |
| C10 | 1.3583892915 | 1.3667551129 | 1.5001891422 |
| H11 | 1.4338701796 | 0.0258043240 | 3.1925507949 |
| H12 | 0.7001570724 | 1.5722703769 | 3.5478122795 |
| H13 | 2.3497169738 | 1.7935192130 | 1.6949949382 |
| H14 | 1.4622817506 | 0.5941330071 | 0.7324793006 |
| H15 | 0.7200502544 | 2.1552235711 | 1.0903884952 |
| C16 | -1.6435047748 | 0.9114315447 | 3.2923589673 |
| C17 | -1.8997615345 | 2.3116908447 | 2.7318599302 |
| H18 | -1.4374695610 | 0.9835399333 | 4.3797071899 |
| H19 | -2.5632636396 | 0.3237740577 | 3.1920096291 |
| H20 | -2.7336534608 | 2.7860619726 | 3.2604478869 |
| H21 | -1.0276435748 | 2.9640034875 | 2.8429656972 |
| H22 | -2.1472731468 | 2.2565275844 | 1.6673262953 |

**$Et_3N$**

| | | | |
|---|---|---|---|
| N1 | -0.6551408176 | 0.2407805109 | 2.4348374216 |
| C2 | -0.7441816064 | -1.2770365004 | 2.5297000734 |

| | | | |
|---|---|---|---|
| C3 | 0.0518183203 | -1.9903570948 | 1.4463539464 |
| H4 | -1.8058198792 | -1.5233557259 | 2.4538255916 |
| H5 | -0.4040013419 | -1.5385839661 | 3.5349642781 |
| H6 | -0.1046710805 | -3.0665135852 | 1.5595210681 |
| H7 | -0.2901437402 | -1.7152863713 | 0.4431701107 |
| H8 | 1.1269626585 | -1.8086874706 | 1.5172334528 |
| C9 | 0.7720499021 | 0.7691163064 | 2.6460179517 |
| C10 | 1.3658112915 | 1.3449178905 | 1.3676267411 |
| H11 | 1.3622588139 | -0.0653095282 | 3.0274585451 |
| H12 | 0.7168408545 | 1.5241113586 | 3.4306705396 |
| H13 | 2.3779996611 | 1.7023937630 | 1.5755865807 |
| H14 | 1.4377861607 | 0.5959656886 | 0.5735997103 |
| H15 | 0.7860959214 | 2.1977295153 | 1.0001668753 |
| C16 | -1.6705415921 | 0.9149031400 | 3.3485673908 |
| C17 | -1.8763904388 | 2.3850105647 | 3.0108129293 |
| H18 | -1.3085187827 | 0.7672546086 | 4.3691887477 |
| H19 | -2.6037092304 | 0.3587373940 | 3.2340261252 |
| H20 | -2.6383062426 | 2.7902038493 | 3.6818908116 |
| H21 | -0.9727311037 | 2.9852448429 | 3.1440703008 |
| H22 | -2.2413477346 | 2.5170135043 | 1.9866780663 |
| H23 | -0.9207671193 | 0.4878681543 | 1.4755765641 |

**[DMF·H]$^{+}$**

| | | | |
|---|---|---|---|
| N1 | 0.0846202903 | 1.7759171483 | -0.0552710883 |
| C4 | 0.6293663337 | 1.0180552258 | -1.2004133977 |
| H5 | -0.0936182359 | 0.2485963918 | -1.4811389530 |
| H6 | 0.8106549240 | 1.6846680575 | -2.0401662448 |
| H7 | 1.5630970190 | 0.5445687435 | -0.8881432792 |
| C7 | -0.2128531841 | 1.0074920280 | 1.1693192774 |
| H8 | -0.9503431394 | 0.2372330544 | 0.9327586126 |
| H9 | 0.7067784355 | 0.5359853841 | 1.5231029683 |
| H10 | -0.6076169916 | 1.6666645973 | 1.9431952742 |
| C10 | -0.1287328286 | 3.0525261924 | -0.1025774963 |
| H11 | -0.5304789265 | 3.5553866375 | 0.7751172330 |
| O12 | 0.1332421879 | 3.7322077696 | -1.1878223822 |
| H13 | -0.0658941666 | 4.6779361431 | -1.0943260793 |

**[DMF]**

| | | | |
|---|---|---|---|
| N1 | -0.0763718458 | 1.7390610119 | -0.2727360878 |
| C4 | 0.6021063135 | 1.0091243691 | -1.3238119579 |
| H5 | -0.0126812406 | 0.1761237399 | -1.6890212613 |
| H6 | 0.8080973239 | 1.6792805299 | -2.1626754872 |
| H7 | 1.5560589216 | 0.5971783146 | -0.9689825532 |
| C7 | -0.4385854345 | 1.0198359596 | 0.9364225119 |
| H8 | -1.1183261643 | 0.1896588919 | 0.7068541286 |
| H9 | 0.4530668832 | 0.6101977453 | 1.4277819659 |

| | | | |
|---|---|---|---|
| H10 | -0.9336770787 | 1.7216304629 | 1.6079156254 |
| C10 | -0.3713550035 | 3.0679147906 | -0.3913288723 |
| H11 | -0.0338874165 | 3.4782579542 | -1.3641097731 |
| O12 | -0.9361826011 | 3.7473974791 | 0.4499081353 |

**Values Calculated by DFT Calculated**

**Relative energies**

| | **HNEt3** | **HDMF** |
|---|---|---|
| | **ΔG (kcal/mol)** | **ΔG (kcal/mol)** |
| **4 endo** | **-0.9** | **-17.1** |
| **4H** | **6** | **-10.2** |
| **4 exo** | **-0.4** | **-16.6** |